Shape Resonances in Photoelectron Spectroscopy

Introduction:

Shape resonances are spectroscopic features that have shown promise for probing the geometry of molecules that are not in the gas phase. For example, shape resonances have been used to determine the orientation of molecules on crystal surfaces. Another possibility is the use of shape resonances as a convenient "ruler" for measuring non-gas-phase molecular bond lengths. If a quantitative relationship between bond length and the energy at which a shape resonance occurs could be established, we would have a powerful analytical tool at our disposal.

What is a Resonance in Quantum Mechanics?

A resonance is a quantum state for which the mean energy lies above the fragmentation threshold of a system and is associated with:

a) a pronounced variation of the cross-section if the fragmentation energy lies in the neighborhood of the energy of the resonance – the width of this neighborhood is called the width of the resonance.
b) a measurable delay of the fragmentation of the system when the system has a mean energy close to the resonance energy – the lifetime (or time delay) of the resonance is proportional to the inverse of its width.

Resonances are usually classified into shape and Feshbach resonances or into Breit-Wigner and Fano resonances.

The classification makes sense only if the lifetimes of the resonances are not larger than the typical vibrational time of the system. Otherwise the situation is much less clear due to overlapping resonances.

What is a Shape Resonance?

A broad resonance or peak in the cross-section of a scattering process that reflects the shape of the potential between projectile and target; this shape consists typically of a barrier separating an inner deep well from a shallow asymptotically vanishing potential at large separation distances.

In quantum mechanics, a shape resonance is a resonance which is not turned into a bound state if the coupling between some degrees of freedom and the degrees of freedom associated to the fragmentation are set to zero.

Of course, in one dimensional systems, resonances are shape resonances. In a system with more than one degree of freedom, this definition makes sense only if the separable model, which supposes the two groups of degree of freedom uncoupled, is a meaningful approximation. When coupling becomes large, the situation is much less clear.

In the case of atomic and molecular electronic structure problems, it is well known that the self-consistent field (SCF) approximation is relevant at least as a starting point of more elaborate methods. The Slater determinants built from SCF orbitals (atomic or molecular) are shape resonances if only one electronic transition is required to emit one electron.

A special kind of shape resonance is core-excited shape resonance.

What is a Feshbach Resonance?

A sharp resonance or peak which is seen when the cross-section of an atomic or nuclear scattering process is plotted as a function of energy. It is associated with an energy threshold above which the scattering process can lead to a new result (such as excitation or ionization of one of the colliding objects), and it lies at an energy slightly below this threshold.

In quantum mechanics, a Feshbach resonance, named after **Herman Feshbach**, in contrast to a shape resonance, is a resonance of a system with more than one degree of

freedom, which would turn into a bound state if the coupling between some degrees of freedom and the degrees of freedom associated to the fragmentation were set to zero.

This definition makes sense only if the separable model, which supposes the two groups of degrees of freedom uncoupled, is a meaningful approximation.

The Slater determinants built from SCF orbitals (atomic or molecular) are Feshbach resonances if more than one electronic transition are required to emit one electron.

Example:

If the ground state of an electronic system can be labeled by a^2p^0 with a a doubly occupied orbital and if f_E corresponds to an incident electron of kinetic energy E, then:

1) $a^2p^0 + f_E \rightarrow a^2p^1$

(Shape Resonance)

2) $a^2p^0 + f_E \rightarrow a^1p^2$ **(with** $a^1p^2 \rightarrow a^1p^1 + f_{E>0}$ **not allowed)**

(Feshbach Resonance)

3) $a^2p^0 + f_E \rightarrow a^1p^2$ **(with** $a^1p^2 \rightarrow a^1p^1 + f_{E>0}$ **allowed)**

(Core Excited Shape Resonance)

In case (1), $\mathbf{a^2p^1}$ is a shape resonance as the $\mathbf{p \rightarrow f_E}$ transition is the only one required for the emission of an electron.

In case (2), $\mathbf{a^2p^1}$ is a Feshbach Resonance, as both transitions $\mathbf{p} \rightarrow \mathbf{f_E}$ and $\mathbf{p} \rightarrow \mathbf{a}$ are required to emit an electron.

In case (3), $\mathbf{a^2p^1}$ is a shape resonance as only the transition $\mathbf{p} \rightarrow \mathbf{f_E}$ is required to emit an electron. This is core-excited shape resonance as one of the fragments is lost in the excited state $\mathbf{a^1p^1}$.

Evidences and Applications of Shape Resonance in PES:

Here we will discuss about the first evidence of shape resonance observed for surface bound acetylene molecules and the inferences that can be obtained from it.

High-resolution symmetry resolved measurements of the C $1s$ photoelectron spectrum of acetylene for photon energies between 297 and 348 eV have been shown to give the energy dependence of the relative cross sections for ionization of the $1\sigma_g$ and $1\sigma_u$ orbitals. The $1\sigma_u^{-1}/1\sigma_g^{-1}$ intensity ratio is greater than 1 at the lowest photon energies but reaches a minimum of about 0.6 between 315 and 320 eV. These results can be understood in terms of the effect of shape resonance on the ionization cross section and provide quantitative information on the position and magnitude of such resonances.

Shape resonances in the core excitation of small molecules have been of considerable interest, especially in light of the suggestion that the position of the resonance above threshold is related to the size of the molecule and, thus, could be used as a ruler to measure molecular dimensions [1].

Subsequent discussion has raised questions about the criteria for establishing that a particular structure in a photoabsorption spectrum is a shape resonance [2].

Kempgens *et al.* have recently concluded that in ethane and ethene there are no readily identifiable shape resonances, and that in ethyne (acetylene) there is only a weak, broad feature at a photon energy of about 312 eV that may be a shape resonance [3].

These observations are important in that these are key molecules in establishing the relationship between bond length and position of the resonance. Thomas *et al* have recently published their new experimental results that allowed them to decompose the cross sections for ethyne reported by Kempgens *et al.* into contributions from $1\sigma_g$ ionization and $1\sigma_u$ ionization. Because of the dipole selection rule, the former is assumed to be associated with outgoing electrons of *u* character and the latter with outgoing electrons of *g* character. The feature seen by Kempgens *et al.* is found to be in a region of high relative probability for $1\sigma_g$ ionization, as would be expected for a σ_u shape resonance. Their results, therefore, lend support to the tentative identification of this feature with the shape resonance. The position of maximum cross section for ionization into the *u* exit channel is at a photon energy of about 310 eV. This is the same as the value of 310 eV proposed by Hitchcock *et al.* [1] for the position of the sigma shape resonance and significantly higher than the value of about 304 eV that has been predicted theoretically [4].

These experimental results also provide a test of theoretical calculations of the photoionization cross section near threshold [4,5] in both the *u* and *g* exit channels. The comparison shows qualitative but not quantitative agreement.

Kempgens *et al.* have shown that the carbon 1*s* photoelectron spectrum of HCCH has a splitting between the $1\sigma_u^{-1}$ **and** $1\sigma_g^{-1}$ states of 105 meV [6]. This large splitting, which is in agreement with theoretical predictions, arises because of the very short bond length of the carbon-carbon triple bond and consequent enhanced overlap of the 1*s* wave functions. Confirming measurements for HCCH and DCCD have been reported by Thomas *et al.* [7].

Using photons from the Advanced Light Source (ALS), they have measured this spectrum at photon energies between 297 and 348 eV. For most of these measurements the resolution is significantly narrower than the natural line width of the carbon 1*s* hole, and this high resolution has allowed them to see features of the photoelectron spectrum that are not readily apparent in the previous results and to gain new insight into the shape resonance.

For photon energies of 300 eV and less, the cross section for the ionization of the $1\sigma_u$ molecular orbital is greater than that for ionization of the $1\sigma_g$ orbital [3]. Their results show that the ratio of the cross sections $1\sigma_u^{-1}/1\sigma_g^{-1}$ decreases as the photon energy increases and goes through a minimum of about 0.6 at a

photon energy of about 317 eV. This energy corresponds roughly to the maximum in what may be the $1\sigma_u$ shape resonance in ethyne [3].
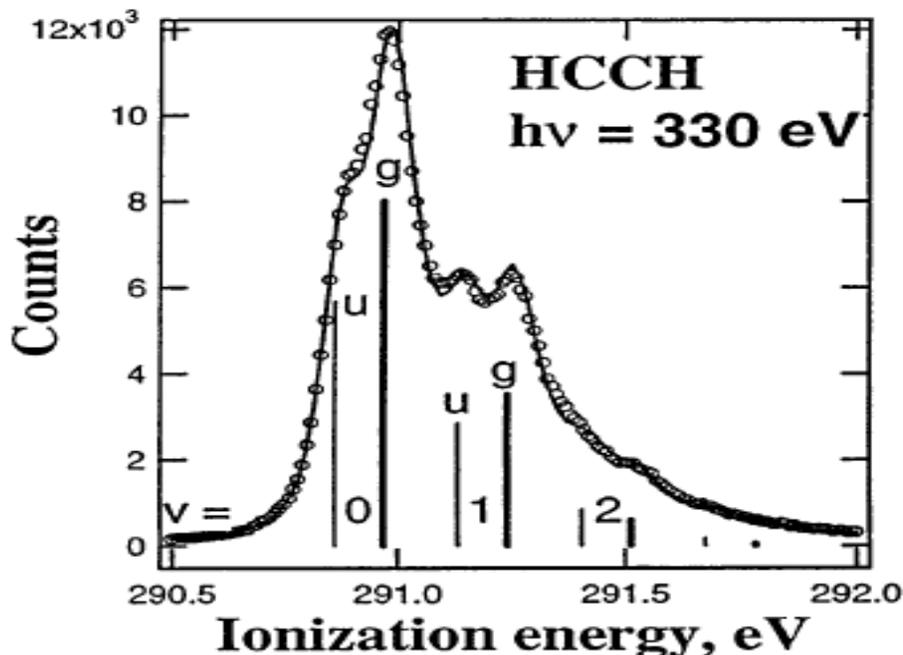

FIG. 1. Carbon $1s$ photoelectron spectrum of HCCH at a photon energy of 330 eV. The points represent the data and the solid curve a fit assuming that carbon-carbon stretching is the only mode contributing to the vibrational structure. The data and the fit extend to both higher and lower energies than shown here. The vertical bars indicate the position and intensity of the different vibrational transitions. The light lines are for $1\sigma_u^{-1}$, and the heavy lines are for $1\sigma_g^{-1}$. The intensities shown for $v = 2$ and $v = 3$ contain contributions from CH stretching modes, which were not considered in the fitting procedure.

The carbon $1s$ spectrum measured for HCCH in the first set of experiments (photon energy of 330 eV and an angle of 54.7^0) is shown in Fig. 1. The data for DCCD are similar but show a distinct peak just above 291 eV because of contributions from CD stretching modes [7]. The principal peak is due to the transition to the vibrational lower ground state of the ion. The most prominent part results from ionization of the $1\sigma_g$ orbital and the shoulder at ionization energy from the $1\sigma_u$ orbital. It is apparent that the cross section for $1\sigma_u$ ionization is less than that for $1\sigma_g$. The u-g split shoulder on the high-energy side of the main peak arises from the $v = 1$ excitation of the carbon-carbon stretching mode. The solid curve shows a fit to the data.
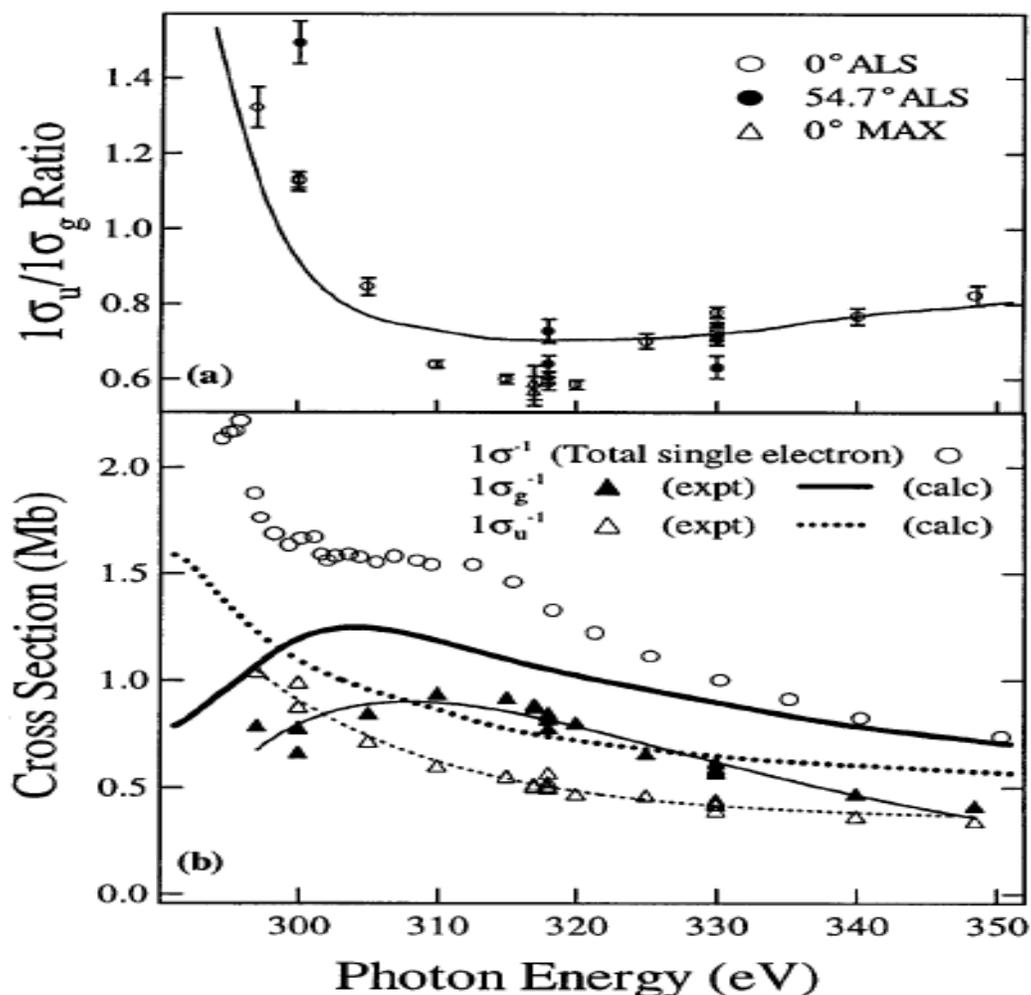
FIG. 2. (a) The ratio of the cross sections for ionization of the $1\sigma_u$ and $1\sigma_g$ electrons of ethyne as a function of photon energy. The open circles represent 0° results for HCCH. The closed circles show 54.7° results for both HCCH and DCCD. The triangles are derived from 0° data for HCCH and DCCD from Ref. [7]. The solid line shows a theoretical calculation from results given in Ref. [5]. (b) Cross section for carbon $1s$ ionization in HCCH. Open circles represent the total single-hole cross section, from Ref. [3]. Triangles show the cross section for ionization of $1\sigma_u$ (open) and $1\sigma_g$ (closed). The heavy solid lines show theoretical results from Ref. [5], and the light lines are smooth curves drawn to show the overall trends more clearly.

The position of the minimum seen in Fig. 2(a) corresponds approximately to a region of high cross section for single-hole [10] ionization of the carbon $1s$ electrons from ethyne, as reported by Kempgens *et al.* [3], and shown as the open circles in Fig. 2(b). These authors have suggested that if there is a shape resonance in ethyne, it is in the region near 312 eV. In N_2, which is isoelectronic with ethyne, x-ray emission spectroscopy [11] indicates that the σ resonance has *u* character. If this is also the case for ethyne, then the resonance provides a mechanism for enhanced emission to the $1\sigma_g^{-1}$ final state. For emission through the σ_u resonance only electrons in the $1\sigma_g$ orbital can participate, since excitation of an electron from $1\sigma_g$ to $k\,\sigma_u$ would be forbidden by the dipole selection rule.

A prominent feature in the photon absorption spectrum at about 310 eV was assigned by Hitchcock *et al.* [1] to the shape resonance. Kempgens *et al.* [3] have concluded that this feature is due primarily to excitation of two-hole, one-particle states in the ionization process, and that a much weaker feature in the single-hole ionization cross section is a possible, though not certain, candidate for the expected resonance. Our measurements have made it possible to decompose their measurements of the total one-hole cross section into components corresponding to $1\sigma_g$ and $1\sigma_u$ ionization. The former, which contains contributions from ionization through the σ_u resonance, shows a maximum also at about 310 eV, and, thus, supports the assignment of a σ_u resonance in this energy region. However, the calculations by Farren [5] indicate that there is also a significant contribution from excitation to a π_u exit channel to this cross section. Thus, although the evidence supports the assignment of a σ_u shape resonance at about 310 eV, it also makes clear, as Kempgens *et al.* [3] have noted, that the assignment of this resonance requires more information than is available in a total cross section measurement.

Many people are familiar with acetylene as a welding fuel, but it also plays an important role in industrial chemistry. Acetylene molecules that are fixed (adsorbed) onto a specially prepared surface serve as the foundation for the synthesis of certain types of plastics, such as polypropylene. To achieve the desired end result, the initial conditions of the acetylene molecules on the surface must be well understood. It would therefore be extremely useful to have a simple way to determine the properties of these molecular building blocks.

The identification of elusive spectroscopic features known as shape resonances, once touted as a tool for measuring molecular bond lengths (see "Significance of a Resonance"), has over the years proven to be controversial. Now, the first convincing evidence for the existence of a shape resonance in acetylene has been obtained at the ALS through high-resolution photoelectron spectroscopy, where small splittings in molecular energy levels can be resolved.

Symmetry-resolved photoelectron spectroscopy measurements taken at the ALS have provided the first convincing evidence for the existence of a shape resonance in acetylene, 15 years after the shape resonance was first proposed.

Shape resonances occur when photoelectrons are temporarily trapped by a potential energy barrier in the molecule. Because the shape of the potential depends upon the configuration of the molecule, it was initially thought that shape resonances might be a simple way to obtain information about molecular geometry. In particular, it was thought that the energy at which a shape resonance occurred could be correlated with the length of molecular bonds.

An attempt was made 15 years ago to quantify the relationship between shape-resonance energy and bond length for a number of molecules, including acetylene. However, shape resonances are manifested as broad, somewhat ambiguous peaks in the photoelectron cross section, and the criteria for identifying shape resonances in general were unclear. Subsequent studies found only weak evidence for a shape resonance in acetylene.

- Predictions of the shape resonances were first done for the diatomic molecules and then extended to the polyatomic ones.
- Experimentally features in the patial photoelectron cross-section curves for the outermost orbital in both CO & N_2 were identified as shape resonances, but evaluation of the comparison was hampered by additional structure in the experimental curve.
- Thus the very strong shape resonance predicted for the fourth band in the photoelectron spectrum of CO_2 was welcomed as an ideal test between theory and experiment.

- Calculations also showed an enormous dip in the angular asymmetry parameter β near 40 eV using a synchrotron radiation. Then it was verified with the experiment showing the Shape Resonance effect.
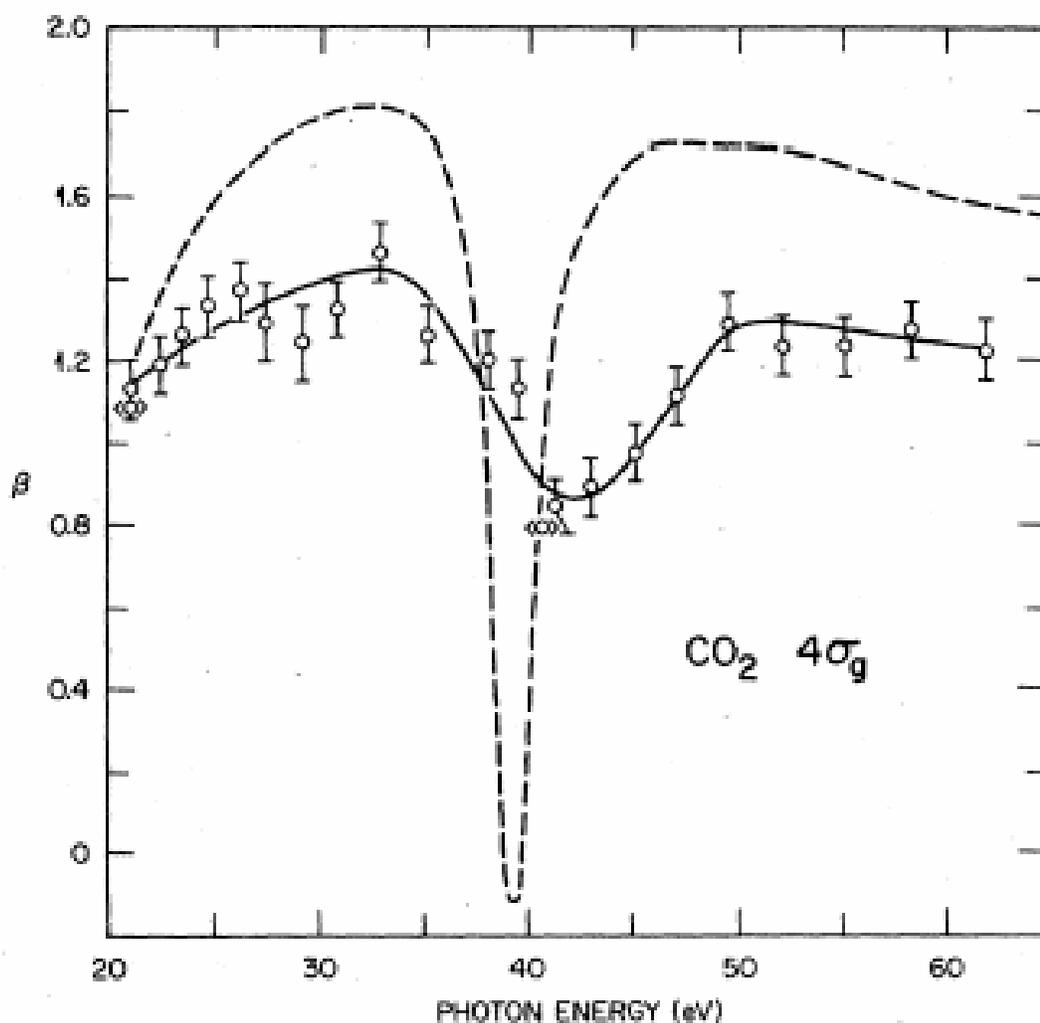

Figure: Angular asymmetry parameter obtained for the fourth band of the photoelectron spectrum of CO_2 representing the $C2\sum g^+$ state of CO_2^+ is plotted as a function of photon energy. Experimental data are given by the open circles with the error bars that reflects the uncertainty in reproducibility. The dashed lines represents the calculated values on the basis of the multiple-scattering method.

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